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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Curable Pulverulent Mixtures

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Notice: This application is as filed and may therefore contain an
incomplete specification.



CURABLE PULVERULENT MIXTURES

Background of the Invention

Powder coatings are used, inter alia, for coating metal furniture such as camping equipment, refrigerators, garden furniture, and shelving, and for coating small objects and workpieces of complex shape, bicycles, sewing machines, and other metal articles. It is largely metal articles which are coated by this process, but powder coating technology can also be used to coat plastics, for example.

Compared with other coating processes, powder coating technology has a number of advantages. For instance, powder coating is a solvent-free operation and is thus environmentally friendly and more cost-effective. The process is also advantageous with regard to waste disposal, workplace safety due to the absence of flammable solvents, industrial hygiene and environmental protection. In addition there is no need to wait for the coats to dry initially. The coated article is conveyed directly to the baking oven, thereby reducing the time expended on the overall coating procedure.

In addition to the production of coatings, powder resins can also be employed as adhesives. This is of advantage if, for example, it is necessary to adhesively bond nonporous materials such as metals from which it is not possible for volatile components to escape subsequently.

However, adhesive systems which are solvent-free and which do not give off elimination products are increasingly being preferred for the processing of porous materials too. These requirements are met by adhesives based on epoxy resins.

Among the heat-curable powder coating systems, it is predominantly epoxy resin combinations which are employed. These epoxy resins are mixed with curing agents, for example with amines, polyamides, acid

anhydrides, boron trifluoride complexes, or dicyandi-
amide. Many of these mixtures have disadvantages which
restrict their industrial application. Both from an
environmental standpoint and given economic
5 considerations, there is currently a requirement for
coating materials and adhesives which are free from
solvent and from elimination products and which can be
processed extremely rapidly.

It has now been found in practice that, for many
10 applications, the curing time of the powder mixtures of
the prior art is too long, since the reactivity of the
known powder mixtures and methods is not sufficiently
high. Thus the powder coating mixture should cure fully
at the lowest possible temperature in the shortest
15 possible time. A further requirement is that of good
storage stability.

The curing of epoxy resins, especially glycidyl
ethers, with numerous anhydrides, di- and polyanhydrides
and various compounds in combination with anhydrides is
20 known (cf. Lee, Neville, Handbook of Epoxy Resins,
McGraw-Hill Book Company, Chapter 12 Acid-Anhydride
Curing Agents for Epoxy-Resins).

As long ago as in the published German Patent
Application D 7193 (September 4, 1952), resinous
25 condensation products were described which comprise
compounds containing ethyleneoxy or propyleneoxy groups
in the molecule and polyanhydrides. According to
published German Patent Application H 9989 (September 10,
1953) synthetic resins can be obtained by heating
30 polyepoxy compounds which contain at least two glycidyl
ether groups and are not derived from phenolic hydroxyl
groups with anhydrides of polybasic carboxylic acids.
From among the plethora of patents, further mention may
be made, for example, of GB-A 744,388, in which mixtures
35 of epoxy resins and hexachloroendomethylenetetrahydro-
phthalic anhydride and the full curing thereof are
disclosed, and of GB-A 1,264,647, which discloses the
curing of epoxy resins with polycarboxylic anhydrides
containing at least one carbocyclic ring in the presence

of acidic polyesters which themselves contain carbocyclic and/or heterocyclic rings.

According to Patent SU 328134, epoxy block copolymers are prepared by condensation of carboxyl-containing compounds with excess epoxide. In this case,
5 linear polyanhydrides of dicarboxylic acids or acidic polyesters are employed as acid component.

Summary of the Invention

Accordingly, it is an object of the invention to
10 provide epoxy compositions of improved storage stability and faster drying time.

It is also an object of the invention to provide methods of making and using such compositions.

It has now surprisingly been found that it is
15 possible, by using specific epoxide compounds, to prepare powder mixtures which are stable on storage and which have a distinctly higher reactivity than the powder resin systems known from the prior art.

In accordance with these objectives, in accordance
20 with a first aspect of the present invention there is been provided a curable pulverulent mixture including:
(A) a compound containing at least two 1,2-epoxide groups which is the reaction product of (A1) a compound having at least two 1,2-epoxide groups per molecule and (A2) a
25 cyclic carboxylic anhydride, and optionally (B) a curing agent.

In accordance with other aspects of the invention, there is provided a substrate coated with a coating obtained by curing a mixture as described above.

30 Further objects, features, and advantages of the invention will become apparent from the details from the detailed description of preferred embodiments that follows.

Detailed Description of the Preferred Embodiments

The epoxide compound (A) employed in accordance with the invention contains on average at least 2 epoxide groups per molecule. Any such compound or mixtures of such compounds prepared using (A1) and (A2) is useful. Epoxy compound (A) may have any desired properties depending on the intended use of the composition.

The epoxide equivalent weight of (A) (molar mass divided by the number of epoxide groups in the molecule) is in general between 300 and 1500 g/mol, preferably between 400 and 800 g/mol and, in particular, between 500 and 700 g/mol, while the acid number is usually from 0.01 to 20 mg of KOH/g, preferably from 0.01 to 2 mg of KOH/g. Furthermore, the epoxide (A) generally possesses a number-average molar mass M_n of from 500 to 10,000 g/mol, preferably from 800 to 3000 g/mol. Depending on the starting components (A1) and (A2) and their molar ratio and on the molar mass of (A), these epoxide compounds are generally solid products having a usual glass transition temperature (T_g) of at least 20°C, preferably from at least 35 to 60°C.

The epoxide compounds (A) are prepared by reacting the compounds (A1) with the cyclic carboxylic anhydrides (A2) in any desired manner, generally by heating the components for several hours with exclusion of oxygen at temperatures from 100 to 200°C, preferably 120 to 160°C, generally until an acid number of less than 20 mg of KOH/g, preferably of 2 mg of KOH/g or less, is reached. In this context it is possible to employ as (A1) both epoxy resins which have been prepared in a one-stage process (for example from bisphenol and epichlorohydrin) and those which are obtainable in a two-stage process (for example from a low molar mass liquid epoxy resin and bisphenol). The epoxide compounds (A) are preferably prepared such that the synthesis of the epoxy resin (A1) is followed immediately by the reaction with the cyclic anhydride (A2).

The 1,2-epoxide compounds employed in accordance with the invention as component (A1) have on average at least two 1,2-epoxide groups per molecule. Any such epoxide compounds or mixtures can be used. Generally the compounds have an epoxide equivalent weight of from 160 to 1000 g/mol, preferably from 160 to 600 g/mol, and a glass transition temperature of at least 10°C and up to 140°C. They may be either saturated or unsaturated and aliphatic, cycloaliphatic, aromatic, or heterocyclic, and may also contain hydroxyl groups. They may additionally contain substituents which do not give rise, under the conditions of mixing or reaction, to any interfering side reactions, examples being alkyl or aryl substituents, ether groups, or the like.

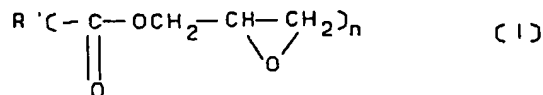
Examples of such polyepoxide compounds (A1) include those based on polyhydric phenols, for example resorcinol, hydroquinone, 4,4'-dihydroxydiphenylmethane, isomer mixtures of dihydroxydiphenylmethane (bisphenol F), 4,4'-dihydroxy-3,3'-dimethyldiphenylmethane, 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), 4,4'-dihydroxydiphenylcyclohexane, 2,2-bis(3-methyl-4-hydroxyphenyl)propane, 4,4'-dihydroxydiphenyl, 4,4'-dihydroxydiphenyl sulfone, tris(4-hydroxyphenyl)methane, 4,4'-dihydroxybenzophenone, 1,1-bis(4-hydroxyphenyl)isobutane, 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane, bis(2-hydroxynaphthyl)methane, 1,5-dihydroxynaphthalene, bis(4-hydroxyphenyl) ether, and also those from the hydrogenation, chlorination and bromination products of the above-mentioned compounds, and from novolaks (*i.e.*, from reaction products of mono- or polyhydric phenols with aldehydes, especially formaldehyde, in the presence of acidic catalysts).

The polyglycidyl ethers of polyhydric alcohols are also suitable as (A1). Examples of such polyhydric alcohols which may be mentioned are trimethylolpropane and 2,2-bis(4-hydroxycyclohexyl)propane.

Also suitable with or as component (A1) are solid acrylate resins which are compatible with any other

components of (A1) and contain glycidyl groups, for example suitable polymers based on glycidyl methacrylate.

Other compounds which are suitable as (A1) are those such as (poly)glycidyl esters of the formula (I)



5 in which R' is a linear or branched, saturated or unsaturated hydrocarbon radical having from 1 up to 40, preferably up to 10, carbon atoms or a substituted or unsubstituted phenyl radical, the substituents being selected from among C₁- to C₈-alkyl and alkoxy radicals
 10 and halogen atoms, and n is at least 2, preferably from 2 to 5. Such polyglycidyl esters of polycarboxylic acids are obtained by reacting epichlorohydrin or similar epoxy compounds with an aliphatic, cycloaliphatic or aromatic polycarboxylic acid, such as oxalic acid, adipic acid,
 15 glutaric acid, terephthalic acid, hexahydrophthalic acid, 2,6-naphthalenedicarboxylic acid and dimerized fatty acids. Examples of these esters are diglycidyl terephthalate and diglycidyl hexahydrophthalate.

Also suitable as polyepoxides (A1) are compounds
 20 such as triglycidyl isocyanurate and its oligomers and triglycidyl urazole and its oligomers, and corresponding mixtures.

These polyepoxide compounds can also be employed as a mixture with one another and, if desired, as a mixture
 25 with monoepoxides, with care preferably being taken to ensure that the mixture of the 1,2-epoxide compounds possesses a glass transition temperature of at least 10°C. If 1,2-epoxide compounds having lower glass transition temperatures are used in the mixture, then
 30 they should preferably be employed only in a minor proportion and only in combination with correspondingly high-melting 1,2-epoxide compounds, so that the glass transition temperature of component (A1) is in the preferred range of at least 10°C.

Examples of suitable monoepoxides include epoxidized monounsaturated hydrocarbons (butylene oxide, cyclohexene oxide and styrene oxide), halogen-containing epoxides, for example epichlorohydrin, epoxide ethers of monohydric
5 alcohols (methyl, ethyl, butyl, 2-ethylhexyl and dodecyl alcohol); epoxide ethers of monohydric phenols (phenol, cresol and other o- or p-substituted phenols); glycidyl esters of unsaturated carboxylic acids, epoxidized esters of unsaturated alcohols or unsaturated carboxylic acids,
10 and the acetals of glycidaldehyde.

Other epoxide compounds having suitable melting points useful in or as component (A1) are described in the handbook "Epoxidverbindungen und Epoxidharze" [Epoxide compounds and epoxy resins] by A.M. Paquin,
15 Springer Verlag, Berlin 1958, Chapter IV, in Lee, Neville "Handbook of Epoxy Resins", 1967, Chapter 2 and in Wagner/Sarx, "Lackkunstharze" [Synthetic resins for coatings], Carl Hanser Verlag (1971), p. 174 ff.

Preferred epoxide compounds (A1) are:

- 20 • poly(epoxyalkyl) ethers of aliphatic or cycloaliphatic polyhydroxy compounds, such as of trimethylolethane, trimethylolpropane, tris(hydroxyethyl) isocyanurate and pentaerythritol;
- reaction products of epihalohydrins such as
25 epichlorohydrin with monomeric polyhydric phenols such as 2,2-bis(4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)ethane, bis(4-hydroxyphenyl)methane, 4,4'-dihydroxydiphenyl sulfone, hydroquinone, resorcinol, dihydroxybiphenyl,
30 dihydroxynaphthalene, and also trisglycidyl isocyanurate;
- glycidyl ethers of polyhydric phenolic compounds, such as novolaks and resols obtained from the condensation of phenol and/or cresols with
35 formaldehyde;
- polyglycidyl esters of polycarboxylic acids, such as diglycidyl esters of phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, polyglycidyl esters derived

from polyesters, or else compounds containing free carboxyl groups.

It is particularly preferred to use as (A1), epoxy resins based on bisphenol A and/or bisphenol F with epichlorohydrin, having epoxide equivalent weights in the range from 160 to 1000 g/mol.

Suitable cyclic carboxylic anhydrides (A2) include any known in the art and are expediently those containing from 4 to 20, and preferably from 4 to 10 carbon atoms, which may if desired also contain substituents such as halogen, especially chlorine, and/or carboxyl groups. They may be derived from (cyclo)aliphatic, olefinically unsaturated or aromatic polycarboxylic acids having 2 or more carboxyl groups. Examples which may be mentioned include succinic anhydride, alkenylsuccinic anhydrides such as, for example, dodecenylsuccinic anhydride, glutaric anhydride, maleic anhydride, citraconic anhydride (methylmaleic anhydride), dichloromaleic anhydride, aconitic anhydride (1-propene-1,2,3-tricarboxylic 1,2-anhydride), tricarballylic anhydride (propane-1,2,3-tricarboxylic anhydride), itaconic anhydride (methylenesuccinic anhydride), cyclopentanetetra-carboxylic dianhydride, Δ^4 -tetrahydrophthalic anhydride, 4-methyl- Δ^4 -tetrahydrophthalic anhydride, hexahydrophthalic anhydride, 4-methylhexahydrophthalic anhydride, 3,6-endomethylene- Δ^4 -tetrahydrophthalic anhydride (= nadic anhydride), 4-methyl-3,6-endo-methylene- Δ^4 -tetrahydrophthalic anhydride (= methylnadic anhydride); 3,4,5,6,7,7-hexachloro-3,6-endomethylenetetrahydrophthalic anhydride (= chlorendic anhydride), the Diels-Alder adduct of 2 mol of maleic anhydride and 1 mol of 1,4-bis(cyclopentadienyl)-2-butene or Diels-Alder adducts of maleic anhydride and conjugated fatty acids such as 2,4-hexadienoic acid (sorbic acid), 9,11-octadecadienoic acid (ricinenic acid), 9,11,13-octadecatrienoic acid (eleostearic acid), 9,11,13,14-octadecatetraenoic acid, and also aromatic polycarboxylic anhydrides such as phthalic anhydride, trimellitic anhydride, pyromellitic

anhydride or benzophenonetetracarboxylic bisanhydride. It is also useful to use other cyclic polycarboxylic anhydrides whose carboxyl groups are on different rings, which may be fused, one example of such compounds being
 5 1,8-naphthalenedicarboxylic anhydride.

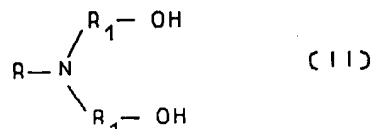
Particular preference is given to succinic anhydride, phthalic anhydride and the cycloaliphatic dicarboxylic anhydrides which can be obtained by Diels-Alder addition from inexpensive petrochemical raw
 10 materials, for example Δ^4 -tetrahydrophthalic anhydride or hexahydrophthalic anhydride.

Components (A1) and (A2) are employed in quantities to give the desired product and are usually employed in quantities such that in general 0.01 - 1 mol, preferably
 15 0.05 - 0.5 mol and particularly preferably 0.1 - 0.4 mol of cyclic anhydride (A2) is used per mole of epoxide compound (A1).

Catalysts can optionally be used in the reaction of (A1) and (A2) to form (A). Examples of catalysts which
 20 can be employed for the targeted and accelerated reaction of the anhydride and/or carboxyl groups of component (A2) and of the epoxide groups of component (A1) include Brönsted bases such as sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium carbonate; chromium
 25 compounds such as CrCl_3 , CrO_3 , chromium acetyl acetonate; imidazoles; quaternary ammonium and phosphonium compounds such as benzyl-trimethylammonium chloride, tetraethylammonium chloride, tetramethylammonium chloride, benzyl-trimethylammonium chloride, benzyl-dodecyl-dimethylammonium
 30 chloride, methyltriphenylphosphonium iodide, triphenyl(2,5-dihydroxyphenyl)phosphonium hydroxide, ethyltriphenylphosphonium acetate, triphenylethylphosphonium bromide and Lewis bases, such as organic phosphines (e.g., triphenylphosphine, tricyclohexylphosphine, tributylphosphine, cyclohexyloctylphosphine)
 35 and amines, which may be aromatic (N,N-dimethylaniline, N,N-diethylaniline, N,N-dimethyl-p-toluidine, N,N-diethyl-p-toluidine) and (cyclo)aliphatic (triethylamine, tributylamine, benzyl-dimethylamine, benzyl-diethylamine,

triethylenediamine, N-methylmorpholine, N-methyl-
piperidine, N-butylamine) as well as alkanolamines such
as diethanolamine, dimethylethanolamine, diethylethanol-
amine, dibutylethanolamine, methyldiethanolamine and
5 di(3-phenoxy-2-hydroxypropyl)alkylamines, for example
di(3-phenoxy-2-hydroxypropyl)-n-butylamine.

Preferred catalysts in this context are those of the
formula (II)



in which

- 10 R = hydrogen, a branched or unbranched alkyl
radical having 1 to 18, preferably 1 to 4,
carbon atoms, a cycloaliphatic alkyl radical
having 5 to 12, preferably 5 to 8, carbon
atoms, or is -R₁OH;
- 15 R₁ = a branched or unbranched alkylene radical
having 2 to 6, preferably 2 or 3, carbon
atoms, which may additionally carry
substituents -OR₂,
- 20 R₂ = a branched or unbranched alkylene radical
having 2 to 6, preferably 2 or 3, carbon atoms
or a substituted or unsubstituted aromatic
ring.

Particularly preferred compounds of the formula (II)
are triisopropanolamine and/or triethanolamine.

25 These optional catalysts when employed, are employed
in a catalytic effective amount and in general in
quantities of from 0.01 to 1%, preferably from 0.05 to
2%, based on the sum of the masses of (A1) and (A2).

30 The reaction products (A) of (A1) and (A2) can be
used in compositions with known epoxy resins, for example
those based on bisphenol A or bisphenol F, in which case
their proportion is preferably allowed to be between 5

and 70% of the overall mass of the epoxide components (A).

Suitable curing agents (B) include all compounds which are known for this purpose, especially anhydride curing agents such as, for example, phthalic anhydride, 5 tetrahydrophthalic anhydride, 4-methyltetrahydrophthalic anhydride, hexahydrophthalic anhydride, 4-methylhexahydrophthalic anhydride, methylnadic anhydride (trivial name for isomers of methylenedimethylenetetrahydrophthalic anhydride), 10 chlorendic (HET) anhydride (3,4,5,6,7,7-hexachloro-3,6-endomethylenetetrahydrophthalic anhydride), pyromellitic dianhydride, benzophenonetetracarboxylic dianhydride, trimellitic anhydride, curing agents in accordance with component (B) of DE-A 25 56 182 (hereby incorporated by reference), 15 dodecenylsuccinic anhydride, isooctenylsuccinic anhydride, other acidic curing agents, dicyandiamide, phenolic curing agents such, for example, as the Dow hardeners ®D.E.H. 80, ®D.E.H. 82, ®D.E.H. 84, carboxylic salts of imidazole or imidazoline compounds, 20 meltable, soluble adducts which are obtained by reacting an epoxide compound with imidazole or imidazoline compounds or the carboxylic salts thereof (cf. DE-C 19 10 758, hereby incorporated by reference).

Polyesters which contain carboxyl groups are 25 preferred as curing agents (B). The epoxide compounds (A) and the carboxyl polyesters as curing agents (B) are present in the mixture according to the invention, in general, in quantities such that the ratio of equivalents of carboxyl groups of the curing agents to epoxide and 30 hydroxyl groups in (A) is from 0.7 to 1.3, preferably from 0.9 to 1.1. For this to apply, the quantity of carboxyl polyesters as curing agent (B) will usually be from 50 to 90%, preferably from 65 to 85%, based on the sum of the masses of (A) and (B). In this way, a sufficient crosslinking density is generally obtained. 35

The carboxyl-containing polyesters employed as component (B) usually possess an acid number of from 15 to 150 mg of KOH/g, preferably from 30 to 100 mg of KOH/g and a glass transition temperature of at least 35°C, pre-

ferably from at least 40 to 60°C. The number-average molar mass M_n (gel chromatography, polystyrene standard) is in general between 600 and 12,000 g/mol, preferably between 2000 and 8000 g/mol. The carboxyl groups are preferably disposed at the ends of the molar chains, which may be linear or branched. The end groups of the carboxyl polyester in general consist of carboxyl groups to the extent of more than 70%, preferably more than 90%. The chain ends preferably predominantly have on average 2 or more carboxyl groups, some of which are present as carboxylic anhydride groups.

The melt viscosities of the carboxyl polyester at 200°C are in general between 1000 and 8000 mPa.s, preferably between 2000 and 6000 mPa.s.

The carboxyl polyesters are prepared in a known manner in a one-stage process or, preferably, in a two-stage process as described, for example, in DE-A 2 163 962 (hereby incorporated by reference), by reacting appropriate polyols with appropriate polycarboxylic acids or derivatives thereof, especially anhydrides. In this context, the polycarboxylic acids and anhydrides are employed in excess. The quantitative ratio is generally such that the ratio of equivalents of hydroxyl to acid and/or anhydride groups is from 1:3 to 1:1.1, preferably from 1:2.2 to 1:1.8.

Compounds which are especially suitable as polyol component include those having hydroxyl numbers in the range from 10 to 80 mg of KOH/g, preferably from 15 to 40 mg of KOH/g, and number-average molar masses M_n (gel chromatography) of from 600 to 10,000 g/mol, preferably from 2000 to 8000 g/mol, and also softening points of from 35 to 110°C, preferably from 40 to 90°C (differential thermal analysis). Examples which may be mentioned here include OH-containing polyesters, polyethers, polythioethers, polyacetals, polycarbonates and polyester-amides. Linear or branched polyesters are preferred in this context.

Examples of such hydroxyl-containing polyesters are reaction products of polyhydric, preferably dihydric and,

if desired, additional trihydric, alcohols with polybasic, preferably dibasic, carboxylic acids. In place of the free polycarboxylic acids it is also possible to use the corresponding polycarboxylic anhydrides or polycarboxylic esters of alcohols having 1 to 6 carbon atoms, mixtures thereof, to prepare the polyesters. The reaction can also be carried out in the presence of conventional esterification catalysts. The polycarboxylic acids may be aliphatic, cycloaliphatic, aromatic and/or heterocyclic in nature and may, if desired, be substituted, for example, by halogen atoms, and/or unsaturated.

Examples of useful carboxylic acids and derivatives thereof for making the polyester curing agents include the saturated aliphatic dicarboxylic acids, succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid; also phthalic acid, isophthalic acid, trimellitic acid, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, tetrachlorophthalic anhydride, endomethylenetetrahydrophthalic anhydride, glutaric anhydride, maleic acid, maleic anhydride, fumaric acid, dimerized and trimerized unsaturated fatty acids, if desired as a mixture with monomeric unsaturated fatty acids, such as oleic acid, and also dimethyl terephthalate and bisglycol terephthalate.

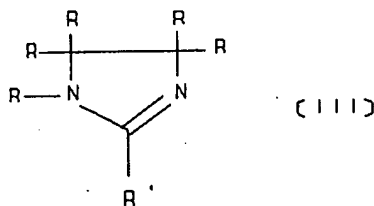
Examples of suitable polyhydric alcohols useful in making the polyester curing agents include ethylene glycol, 1,2- and 1,3-propylene glycol, 1,4- and 2,3-butyleneglycol, 1,6-hexanediol, 1,8-octanediol, neopentylglycol, 1,4-bishydroxymethylcyclohexane, 2-methyl-1,3-propanediol, glycerol, trimethylolpropane, 1,2,6-hexanetriol, 1,2,4-butanetriol, trimethylolmethane, pentaerythritol, quinitol, mannitol and sorbitol, methylglycoside, and also diethylene glycol, triethylene glycol, tetraethylene glycol and higher polyethylene glycols, dipropylene glycol and higher polypropylene glycols, and dibutylene glycol and higher polybutylene glycols. It is also useful to employ polyesters of lactones, for example, ϵ -caprolactone, or of hydroxycarboxylic acids, for example, α -hydroxycaproic acid.

Examples of the anhydrides useful as curing agents (B) are, in particular, trimellitic anhydride (TMAA) and pyromellitic anhydride or maleic anhydride adducts with, for example, piperylene.

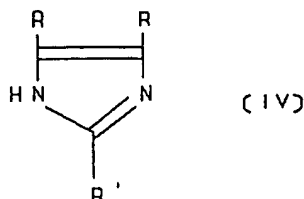
Further carboxyl-containing polyesters which are suitable in accordance with the invention as curing agents (B) are, for example, those described in DE-C 36 18 355 and in DE-A 21 63 962, and 26 18 729, each of which are hereby incorporated by reference.

Particularly preferred curing agents are carboxyl-containing polyesters whose acid number is between 15 and 150 mg of KOH/g and whose number-average molar mass is between 600 and 12,000 g/mol.

Other preferred curing agents are imidazolines of the formula (III)



in which each substituent R, independently of the others, is hydrogen or a C₁ to C₂₀-alkyl, aryl, aralkyl, cycloalkyl or heterocyclic radical, R' is the same as R or is an alkylene or arylene radical connecting two imidazole or imidazoline groups, any of R and R' may possibly be substituted by one or more C₁ to C₂₀-alkyl, aryl, aralkyl, cycloalkyl or heterocyclic radicals, and where two or more radicals may be connected, possibly also by heteroatoms, and/or imidazoles of the formula (IV)



in which R and R' are as defined for formula (III).

Examples of suitable imidazolines include the following compounds: 2-methylimidazoline, 2-ethyl-4-methylimidazoline, 2-phenylimidazoline, 2-undecylimidazoline, 2-heptadecylimidazoline, 2-ethylimidazoline, 2-isopropylimidazoline, 2,4-dimethylimidazoline, 2-phenyl-4-methylimidazoline, 2-benzylimidazoline, 2-(o-tolyl)imidazoline, 2-(p-tolyl)imidazoline, tetramethylenebisimidazoline, 1,1,3-trimethyl-1,4-tetramethylenebisimidazoline, 1,3,3-trimethyl-1,4-tetramethylenebisimidazoline, 1,1,3-trimethyl-1,4-tetramethylenebis-4-methylimidazoline, 1,2-phenylenebisimidazoline, 1,3-phenylenebisimidazoline, 1,4-phenylenebisimidazoline and 1,4-phenylenebis-4-methylimidazoline. It is also useful to employ any desired mixtures of the imidazolines.

Examples of suitable imidazoles include imidazole itself, 1-methylimidazole, 2-methylimidazole, 4-methylimidazole, 5-methylimidazole, 1-ethylimidazole, 2-ethylimidazole, 1-propylimidazole, 2-propylimidazole, 2-isopropylimidazole, 1-butyylimidazole, 2-octylimidazole, 2-undecylimidazole, 2-heptadecylimidazole, 2-cyclohexylimidazole, 1-phenylimidazole, 2-phenylimidazole, 2,4-dimethylimidazole, 1,2-dimethylimidazole, 4,5-dimethylimidazole, 2-ethyl-4-methylimidazole, 1-ethyl-2-methylimidazole, 1-methyl-2-isopropylimidazole, 4-butyl-5-ethylimidazole, 2-cyclohexyl-4-methylimidazole, 1-benzyl-2-methylimidazole, 2-phenyl-4-methylimidazole, 4,5-diphenylimidazole, 2-ethyl-4-phenylimidazole, 2,4,5-trimethylimidazole, 2,4,5-tricyclohexylimidazole, 1,2,4,5-tetramethylimidazole and benzimidazoles and derivatives thereof. It is also useful to employ any desired mixtures of the imidazoles and/or imidazolines.

The quantity of curing agents in the pulverulent mixtures according to the invention depends on the nature of the curing agent and can fluctuate within wide limits to give the desired curing. The quantity of curing agent is generally from 0.01 to 90%, preferably from 0.5 to 85%, based on the sum of the masses of the two components

(A) and (B). In the case of imidazoles or imidazolines, a mass fraction of 0.01 to 70%, preferably of 0.5 to 40%, of curing agent in the composition is usually chosen.

5 In addition to components (A) and (B), the mixtures according to the invention may contain additives which are conventional for powder coatings, such as leveling agents or anticrater agents, dyes, pigments, fillers, matting agents, thixotropic agents, deaerating agents, UV
10 stabilizers, oxidation inhibitors, quenchers (free-radical scavengers, for example, N-alkyl-substituted piperidines), catalysts for accelerating the crosslinking reaction, plasticizers, additional curing agents, additional curable resins, and the like. Any of these additives or mixtures thereof can be used. These additives
15 are generally employed in effective quantities of from 0 to 50%, preferably from 0.1 to 40%, based on the overall mass of the powder coating mixture. Any liquid or pasty additives here can be used, inter alia, as a mixture with highly active silicic acid as a masterbatch (see
20 DE-A 22 02 907).

Leveling agents which can be employed include, for example, acetals such as polyvinylformal, polyvinylacetal, polyvinylbutyral, polyvinylacetobutyral, and the like, polyethylene glycols and polypropylene glycols,
25 silicone resins, mixtures of zinc soaps, of fatty acids and aromatic carboxylic acids, and in particular commercially available products based on polyacrylates. The leveling agents can be added to component (A) in effective quantities, for example, of from 0.1 to 4%, preferably from 0.2 to 2.0%.
30

Examples which may be mentioned of the dyes or pigments, which may be inorganic or organic in nature, are titanium dioxide and zinc oxide. The organic dyes or pigments should of course be selected such that they are
35 stable at the curing temperatures and do not lead to any intolerable alterations in shade.

Examples of suitable fillers include ground quartz, silicates, chalk and gypsum.

The stabilizers can be aromatic diketones such as benzoin, which prevent localized decomposition and thus suppress the formation of pores.

5 The stabilizers are generally added in quantities of from 0.1 to 3%, preferably from 0.2 to 2%, based on the mass of the overall binder mixture.

10 In order to prepare the pulverulent mixtures according to the invention for testing, processing and practical application, the individual components are generally mixed with one another. When using liquid constituents, generally the solid components are finely ground and the liquid components are distributed uniformly therein. In order to prepare the curable mixtures according to the invention, the components are homo-
15 genized in the melt after mixing. This can take place in suitable equipment, for example, heatable kneading apparatus, double-Z mixers, or extruders, preferably the latter, the extrusion temperature being chosen such that maximum shear force acts on the mixture. In this con-
20 text, an upper temperature limit of 130°C should not be exceeded. When using catalysts it may be advantageous to add these to component (A) or (B). This addition can also be made, for example, during the preparation of component (A).

25 The homogenized mass is then allowed to cool to room temperature and, after suitable precomminution, is ground to give a curable, pulverulent mixture (powder coating). The target average particle sizes depend on the intended use and are generally from about 40 to 90 μm , but pre-
30 ferably about 50 μm . Any oversize present, with a particle size of more than 90 μm , is generally removed by screening.

On the basis of their high reactivity, the mixtures according to the invention are particularly suitable as
35 adhesives and coating compositions. The mixture can be made solvent free, thereby achieving the advantages mentioned at the outset.

The powder coatings thus produced can be applied to suitable substrates, for example, metal, wood, glass,

concrete, plastic and ceramic, by known methods, for example, by electrostatic powder spraying, powder application by the triboelectric method, fluidized-bed sintering, electrostatic fluidized-bed sintering or by flame spraying.

After the powder coating has been applied by one of the methods mentioned, the coated workpieces are generally heated, to achieve full cure, to a temperature of from 90 to 270°C, preferably from 120 to 220°C, for a time which is sufficient to achieve full curing, in general from 0.5 to 60 minutes. The resulting coatings are distinguished by good properties in terms of paint technology, such as good mechanical properties, good chemical resistance, good weathering resistance and good adhesion. The powder coatings according to the invention are consequently suitable, in particular, for coating materials such as, for example, metal, glass, fabrics, paper, and ceramic.

In addition to the use as coatings, the mixtures according to the invention can also be employed as adhesives. The production of adhesive formulations is in principle carried out in the same way as described for the powder coating mixtures. In other words the solid epoxy resins (component A) are first comminuted and then intimately mixed with the curing agent (B), care being taken to ensure uniform distribution of the components.

The formulations thus obtained may if desired be admixed with conventional additives as described above, such as fillers, pigments, and/or dyes. The mixtures according to the invention can be used for adhesive bonding of all types of materials, for example, metals, light metals, but also nonmetallic materials such as ceramic, glass, leather, rubber, paper, cardboard, wood and plastics with themselves or with other materials. They can also be employed in the preparation of sandwich constructions of metals and other materials.

A point worthy of particular emphasis is the possibility of constructing sandwich systems from wood (chipboard, plywood, etc.) and fabrics, for example,

polyester fibers (*Trevira). In the course of the
adhesion process the fabric is embedded completely in the
binder system, forms a homogeneous surface and adheres in
an optimum manner to the substrate. The laminate
5 obtained in this way, even with a lower thickness of
material, has a high flexural strength in relation to
plain chipboard or plywood panels. This procedure makes
it possible to obtain panels which, while of the same
quality, are of lower weight in comparison to standard
10 materials.

When the mixtures according to the invention are
used for adhesive bonding they can be applied by
electrostatic means, for example, with an electrostatic
powder spray gun. In this way it is possible to apply
15 uniformly thin coats, for example, on films. Because of
the rapid reaction of the individual components of the
mixtures according to the invention at low temperatures,
it is also possible to achieve high rates of production
throughput.

20 An outstanding advantage in this application means
is that yellowing, combustion, and gas escape can be
avoided. The pulverulent mixture on the coated materials
generally cures fully at temperatures of from 120 to
220°C, preferably from 130 to 210°C, in an adequate time
25 of from 2 to 60 minutes.

The compositions according to the invention are
particularly suitable for the coating of filter papers
which can be used in the production of filters for low-
and medium-viscosity liquids, for example, oils. In this
30 case either the epoxy resin/curing agent mixture is
applied to untreated filter paper in the form of a fine
powder and incipiently melted for a brief period, or the
paper is coated with a melt of the mixture. Full curing
is then carried out at the stage of ultimate fabrication
35 and adhesive bonding.

The present invention is further illustrated by the
following examples, which are for illustrative purposes
only and do not limit the invention.

EXAMPLES:

Epoxy resin I (comparison)

Commercially available bisphenol A epoxy resin for the preparation of powder coatings, having the following characteristics:

5	Epoxy resin I (comparison)	
	Epoxide equivalent weight	about 800 g/mol
	Viscosity at 25°C	about 500 mPa.s
	40% strength in butyldiglycol	
	in accordance with DIN 53 015	
10	Melting point	about 70°C
	Capillary method in accordance	
	with DIN 53 015	
	Glass transition temperature	about 50°C

Epoxy resin II (according to the invention)

15 Preparation

1464 g of a liquid bisphenol A epoxy resin having an epoxide equivalent weight of 183 g/mol (8 mol of epoxy groups) and 456 g of bisphenol A (2 mol) are heated to 125°C in a four-necked flask with stirring under a
20 nitrogen atmosphere, and 4 g of triethanolamine are added. By exothermic reaction and additional heating, the temperature is brought to 160°C over the course of 15 minutes and maintained for 4.5 hours. The epoxide equivalent weight is then 468. After a holding time of
25 a further hour at 160°C, the temperature is reduced to 150°C and 91.4 g (0.6 mol) of tetrahydrophthalic anhydride are added. After 1.25 hours, the acid number is 0.9 mg of KOH/g. After a further 0.5 hour, the flask is emptied.

30 Characteristics:

Epoxide equivalent weight	601 g/mol
Acid number (toluene/ethanol)	0.2 mg of KOH/g
Viscosity 25°C (40% in butyldiglycol	519 mPa.s
Glass transition temperature	45.7°C

Example 1

Gel time determination

5 The gel time was measured in accordance with
DIN 16 916 Part 2 (September 1987) section 5.7.1,
"Determination of the B-stage time", at 180°C. The
results for various mixtures according to the invention
in comparison with those of the prior art are listed in
Table 1.

10 The pulverulent mixtures according to the invention
exhibit surprisingly short gel times in comparison with
the mixtures containing a prior art epoxy resin. This is
a measure of the high reactivity of the mixtures accord-
ing to the invention which are used, and demonstrates the
great influence of the epoxy resin component A on the
15 rate of reaction of the overall system.

Table 1: Gel time determinations at 180°C

	Epoxy resin	Curing agent	Parts by wt. (pbw) of curing agent per 100 pbw of epoxy resin	Seconds
5	I	2-Heptadecylimidazole	0.5	> 600
	II	2-Heptadecylimidazole		130
	I	2-Heptadecylimidazole	1	> 600
	II	2-Heptadecylimidazole		62
	I	2-Heptadecylimidazoline	2.5	725
	II	2-Heptadecylimidazoline		172
10	I	2-Ethyl-4-methylimidazoline	1	219
	II	2-Ethyl-4-methylimidazoline		35
	I	2-Methylimidazoline	1	282
	II	2-Methylimidazoline		111
15	I	2-Phenylimidazole	2.5	85
	II	2-Phenylimidazole		37
	I	2-Phenylimidazoline	2.5	337
	II	2-Phenylimidazoline		103
	I	Curing agent B31 (Hüls)	1	> 600
	II	Curing agent B31 (Hüls)		376
20	I	Curing agent B31 (Hüls)	2.5	324
	II	Curing agent B31 (Hüls)		79
	I	Curing agent B68 (Hüls)	2.5	> 600
	II	Curing agent B68 (Hüls)		221
25	I	Curing agent B55 (Hüls)	2.5	> 600
	II	Curing agent B55 (Hüls)		190
	I	Curing agent EH 694 (Hoechst)	15	234
	II	Curing agent EH 694 (Hoechst)		80
	I	Trimellitic anhydride	6	587
	II	Trimellitic anhydride		108
30	I	Pyromellitic anhydride	5	314
	II	Pyromellitic anhydride		112
	I	Dicyandiamide	2.5	684
	II	Dicyandiamide		280
35	I	Dyhard® 100 (SKW Trostberg)	2.7	623
	II	Dyhard® 100 (SKW Trostberg)		225

Curing agent B31: cyclic amidine
 Curing agent B55: } salt of a polycarboxylic acid and of a
 Curing agent B68: } cyclic amidine
 Curing agent EH694: resinous anhydride
 Dyhard® 100: dicyandiamide

Example 2

Coatings testing

The powder coatings tested in Table 3 were prepared by extruding the powder coating mixtures comprising carboxyl polyester, epoxy resin, pigment and additives in the mixing ratio given in Table 2 and are comparable with one another in respect of the preparation process and the particle size distribution (average particle size 50 μm). The extruded powder coating mixtures were applied to degreased steel panels using a Corona spray gun. The coating thickness was on average about 63 μm and the stoving temperature was 160°C (see Table 3). The tests were carried out in accordance with the standards indicated.

The tendency toward yellowing was determined by dividing the coated panels together with the baked films and overbaking one half at 200°C. The ΔE color difference measurement was carried out on a Tricolor LFM 3 colorimeter from Lange in accordance with DIN 6174, CIE-LAB 1976, against a white standard or, in the case of the overbaked films, against the portion of the film which was not overbaked.

Table 2: Powder coating mixtures (composition in parts by weight)

	Example 2 a) Comparison	Example 2 b)
Epoxy resin I	170	-
Epoxy resin II	-	157
Polyester ¹⁾	397	410
Titanium dioxide ²⁾	300	300
Blanc fixe F	100	100
Leveling agent ³⁾	30	30
Benzoin	3	3

- 5
- 10 1) Carboxyl polyester® Alftalat AN 770 (Hoechst) having the following characteristics:
- Acid number (DIN 53 402): 34 ± 4 mg of KOH/g
- Glass transition temperature: 53 ± 2°C
- (measured by DSC, Mettler TA 3000, at 10°C/min)
- 15 Viscosity at 200°C: 5,000 to 6,500 mPa.s
- (measured with ICI Cone & Plate)
- 2) ®Kronos 2160 from Kronos Titan
- 3) ®Additol XL 396 (Hoechst)

Table 3: Test results for the coating films

		Example 2c (Comparison)	Example 2d (Comparison)	Example 2e	Example 2f
	Powder coating mixture example	2a	2a	2b	2b
	Drying temperature (°C)	160	Overbaking 200	160	Overbaking 200
5	Drying time (min)	10	60	10	60
	Coat thickness (μm)	60 - 66	56 - 62	60 - 66	66 - 70
	Gloss 60° perspective DIN 67 530 (%)	95	94	95	94
	Leveling (+)	2		2	
10	Cratering (+)	0		0	
	Erichsen indentation DIN 53 156 (mm)	11.2	11.8	11.5	11.7
	Impact testing ASTM D 2794				
15	direct Nm (lb-in)	1.8 (16)	18.1 (160)	6.8 (60)	18.1 (160)
	indirect NM (lb-in)	<0.5 (<4)	18.1 (160)	4.5 (40)	18.1 (160)
	Butyl acetate test 3 min (+)	5	4	4	3
	Xylene test 30 min (+)	5	5	5	4
20	ΔE rel. to powder white standard	1.21		1.35	
	ΔB rel. to powder white standard	0.12		0.04	
	ΔE rel. to normal curing		3.15		1.94
25	ΔB rel. to normal curing		2.79		1.93
	Blocking resistance of the powder coating mixture 40°C acc. to DIN 55990 7 days	2		2	
30	Gel time of the powder coating mixture at 180°C (s)	197		85	

(+) = visual assessment in accordance with DIN 53 230

0 = very good, 5 = very poor

From the examples in Table 3 it is evident that the powder coating films of the powder coating mixture according to the invention give test results which are equal to (gloss, leveling, cratering, Erichsen indentation) and in some cases better than (solvent test, yellowing resistance) those of the comparison powder coating mixture. In particular, the powder coating mixture 2 b (2 e) according to the invention exhibits substantially greater reactivity (lower gel time) than that of the prior art 2 a (2 c). Furthermore, it was found that the impact testing values of the coating film according to the invention (2 e) at the chosen baking temperature are higher than those of the comparison (2 c). In practice, therefore, powder coating films can advantageously be stoved at lower temperatures with the resins according to the invention than with those according to the prior art.

Example 3

Bonding of polyester fabric

The resin/curing agent mixture (e.g., 92 parts by weight of epoxy resin II and 8 parts by weight of curing agent B 31, cyclic amidine from Hüls Aktiengesellschaft) is mixed in an MTI mixer to a particle size of < 5 mm and extruded at 80°C with a residence time of 10-15 seconds, and the liquid melt of the binder/curing agent mixture, directly after the dispersion in the extruder, is passed together with the polyester fabric through a calender, in the course of which operation the liquid melt material is distributed uniformly on the fabric. The coated fabric is stored at ambient temperature prior to its subsequent use or adhesive bonding.

The fabric treated with the powder mixture is punched out, cut and then adhesively bonded with chipboard panels under a pressure of 40 bar over 40 seconds at 200°C. Under the process conditions chosen, the powder mixture melts, wets the substrate (chipboard and fabric) very thoroughly and then cures fully. In

this procedure the polyester fabric is completely embedded in the binder system, forms a homogeneous surface and adheres to the substrate in an optimum manner.

5 **Example 4**

Bonding of polyester fabric

 The resin/curing agent mixture (e.g., 92 parts by weight of epoxy resin II and 8 parts by weight of curing agent B 31, cyclic amidine from Hüls Aktiengesellschaft) is mixed in an MTI mixer to a particle size of < 5 mm and is extruded at 80°C with a residence time of 10-15 seconds. The extrudate emerging at 100°C is cooled, broken, ground and screened to a particle size of < 125 µm.

15 The powder mixture obtained in this way is applied using an electrostatic powder spray gun to polyester fabric and the coated material is processed further either by

- 20 a) immediately pressing and adhesively bonding the polyester fabric provided with the powder mixture onto chipboard to be laminated, or by
- b) fusing the powder mixture for 2 minutes at 100°C onto the Trevira fabric, placing the material in intermediate storage and then adhesively bonding it to chipboard.

25 The adhesive bonding of the fabric treated in this way is carried out under pressure (40 bar) over 40 seconds at 200°C to chipboard. Owing to the chosen process conditions, the powder mixture melts, wets the substrate (chipboard and fabric) very thoroughly and then cures fully.

Example 5

Filter paper coating

35 The epoxy resin/curing agent mixture (e.g., 92 parts by weight of epoxy resin II and 8 parts by weight of curing agent B 31, cyclic amidine from Hüls Aktiengesellschaft) is mixed in an MTI mixer to a

particle size of < 5 mm and is extruded at 80°C with a residence time of 10-15 seconds. The extrudate emerging at 100°C is cooled, broken, ground and screened to a particle size of < 125 μ m.

5 The powder mixture obtained in this way is applied using an electrostatic powder spray gun to filter paper, fused to the paper at about 100°C for 2 minutes, and placed in intermediate storage until adhesive bonding is carried out.

10 An alternative procedure which is possible is to cut the filter paper, which has been provided with the as yet unfused powder coating, to the desired shape, to punch it out and then immediately to carry out adhesive bonding.

15 Instead of the electrostatic application, the liquid melt of the binder-curing agent mixture can be applied directly, following its dispersion in an extruder, to the paper. To this end the liquid material is passed together with the filter paper through a calender, resulting in a uniform coat on the paper. The coated
20 filter paper is then placed in intermediate storage until adhesive bonding is carried out.

25 The papers treated with the powder coating are punched out to shape, cut and then bonded to one another under pressure and with heating. Owing to the chosen process conditions, the powder melts, sufficiently wets
30 the papers to be bonded and cures in a very short time (e.g., a few seconds at 180°C) to give adhesive bonds which are suitable for the production of oil filters.

30 While the invention has been described with reference to certain preferred embodiments, numerous modifications, alterations, and changes to the preferred embodiments are possible without departing from the spirit and scope of the invention.

What Is Claimed Is:

1. A curable pulverulent mixture comprising
 - (A) a compound containing at least two 1,2-epoxide groups which is the reaction product of
 - (A1) a compound having at least two 1,2-epoxide groups per molecule and
 - (A2) a cyclic carboxylic anhydride, and
 - (B) optionally a curing agent.
2. A curable mixture as claimed in claim 1, wherein the compound (A1) has an epoxide equivalent weight of between 160 and 1000 g/mol.
3. A curable mixture as claimed in claim 1, wherein the compound (A1) is selected from the group consisting of the diglycidyl ethers of bisphenol A and bisphenol F.
4. A curable mixture as claimed in claim 1, wherein the cyclic anhydride (A2) is selected from the group consisting of succinic anhydride, phthalic anhydride, Δ^4 -tetrahydrophthalic anhydride, and hexahydrophthalic anhydride.
5. A curable mixture as claimed in claim 1, wherein the compound (A) has an epoxide equivalent weight of from 300 to 1500 g/mol.
6. A curable mixture as claimed in claim 1, wherein the glass transition temperature of the compound (A) is at least 20°C.
7. A curable mixture as claimed in claim 1, wherein the compound (A) has an acid number of from 0.01 to 20 mg of KOH/g.

8. A curable mixture as claimed in claim 1, wherein the compound (A) has a number-average molar mass of from 500 to 10,000 g/mol.

9. A curable mixture as claimed in claim 1, wherein to synthesize component (A), from 0.01 to 1 mol of cyclic carboxylic anhydride (A2) is employed per mole of epoxide compound (A1).

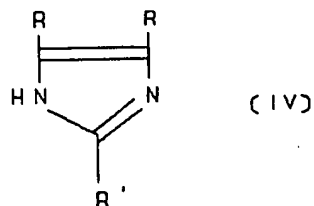
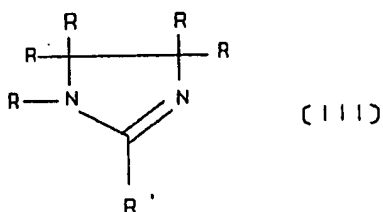
10. A curable mixture as claimed in claim 1, wherein to synthesize component (A), from 0.05 to 0.5 mol of cyclic carboxylic anhydride (A2) is employed per mole of epoxide compound (A1).

11. A curable mixture as claimed in claim 1, wherein a curing agent (B) is present which comprises a carboxyl-containing polyester.

12. A curable mixture as claimed in claim 11, wherein the acid number of the carboxyl-containing polyester is from 15 to 150 mg of KOH/g.

13. A curable mixture as claimed in claim 11, wherein the number-average molar mass M_n of the carboxyl-containing polyester is between 600 and 12,000 g/mol.

14. A curable pulverulent mixture as claimed in claim 1, wherein a curing agent (B) is present which comprises an imidazoline of the formula (III) or an imidazole of the formula (IV),



in which each radical R, independently of the others, is hydrogen or an alkyl, aryl, aralkyl, cycloalkyl, or heterocyclic radical,

R' is the same as R or is an alkylene or arylene radical;

wherein R and R' may optionally be substituted by one or more alkyl, aryl, aralkyl, cycloalkyl or heterocyclic radicals, and

where two or more radicals may be connected, optionally by heteroatoms.

15. A curable mixture as claimed in claim 14, wherein curing agent (B) is present and comprises 2-phenylimidazoline.

16. A curable mixture as claimed in claim 1, wherein curing agent (B) is present and comprises dicyandiamide.

17. A curable mixture as claimed in claim 1, wherein the quantity of curing agent (B) is from 0.01 to 90%, based on the sum of the masses of (A) and (B).

18. A substrate coated with a coating obtained by curing a mixture as claimed in claim 1.

19. An adhesive comprising a curable mixture as claimed in claim 1.

20. Filter paper coated with a curable mixture as claimed in claim 1.

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Abstract of the Disclosure

A curable pulverulent mixture including (A) a compound containing at least two 1,2-epoxide groups which is the reaction product of (A1) a compound having at least two 1,2-epoxide groups per molecule and (A2) a cyclic carboxylic anhydride, and optionally (B) a curing agent, is useful, for example, in adhesive and coating compositions.

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